Russian Journal of Applied Chemistry, Vol. 75, No. 2, 2002, pp. 219–222. Translated from Zhurnal Prikladnoi Khimii, Vol. 75, No. 2, 2002, pp. 227–230. Original Russian Text Copyright © 2002 by Medvedev, Makrushin, Dubenkov.

> APPLIED ELECTROCHEMISTRY AND CORROSION PROTECTION OF METALS

Electrodeposition of Tin from Sulfate Electrolyte in the Presence of Synthanol, Formalin, and Propargyl Alcohol

G. I. Medvedev, N. A. Makrushin, and A. N. Dubenkov

Novomoskovsk Institute of Mendeleev Russian University of Chemical Technology, Novomoskovsk, Russia

Received July 26, 2001

Abstract—The process of electrodeposition of tin from a sulfate electrolyte containing $SnSO_4$, H_2SO_4 , synthanol, formalin, and propargyl alcohol was studied.

Previously, electrodeposition of tin from a sulfate electrolyte in the presence of organic additives has been studied [1, 2]. It was shown that electrodeposition in an electrolyte containing synthanol and formalin, together with 1,4-butanediol and 2-butene- and 2-butyne-1,4-diols, yields lustrous coatings. The present communication reports the results obtained in studying electrodeposition of tin from a sulfate acid electrolyte in the presence of synthanol, formalin, and propargyl alcohol.

The investigation was carried out in an electrolyte containing (g I^{-1}): SnSO₄ 10–50, and H₂SO₄ 90–100. The organic substances were introduced into the electrolyte in the following amounts: synthanol (DS-10) 1–4 g I^{-1} , formalin (37% solution) 1–10 ml I^{-1} , and propargyl alcohol 1–15 ml I^{-1} .

Tin was deposited onto copper substrates to a thickness of $6-15 \mu m$. Polarization curves were measured with a P-5828 potentiostat. The luster was measured with an FB-2 photoelectric luster meter. The degree θ of surface coverage with organic additives was evaluated by the results of polarization measurements, using the formula [3]

$$\theta = 1 - \exp(\Delta E/b),$$

where ΔE is polarization, and *b* is the constant appearing in the Tafel equation, determined from polarization curves plotted in the ΔE -log i_c coordinates.

The leveling power P of the electrolytes was determined directly by profilometric measurements of the surface of samples with sinusoidal microprofile. The P value was calculated using the formula [4]:

$$P = 2.3a/2\pi h_{\rm av} \log(H_0/H_i),$$

where *a* is the wave amplitude of the sinusoidal microprofile; h_{av} the average coating thickness (10 µm); and H_0 and H_i the initial and final amplitudes of the sinusoidal microprofile, respectively.

The capacitance of the electric double layer was measured in the course of electrolysis with a P-5021 ac bridge at a frequency of 30 kHz, using the series equivalent scheme.

The electrodeposition was done at 18–25°C with and without electrolyte agitation by means of a magnetic rabble.

The effect of organic additives on the outward appearance of coatings was studied in an electrolyte containing 50 g l⁻¹ SnSO₄ and 100 g l⁻¹ H₂SO₄. It was found that, with synthanol (1–4 g l⁻¹) added to the electrolyte, dull coatings are obtained. With formalin (1–10 ml l⁻¹), or propargyl alcohol (1–15 g l⁻¹), or a mixture of these, poor-quality coatings are deposited. The outward appearance of coatings is much improved if propargyl alcohol is added to an electrolyte containing synthanol (2–3 g l⁻¹) and formalin (6–8 ml l⁻¹). Data on the influence exerted by propargyl alcohol on the outward appearance of the coatings are presented in the table.

It can be seen that lustrous coatings are obtained in the presence of propargyl alcohol. The widest range of current densities at which lustrous coatings are obtained ($i_c = 7-12 \text{ A dm}^{-2}$) is observed at propargyl alcohol concentrations of 7–10 ml l⁻¹.

With the formalin concentration outside the above limits, silvery coatings are obtained. At synthanol

$c_{\rm pa}^{,**}$ ml l ⁻¹	i, A dm ⁻²	Outward appearance of coatings
1–3	1–5	Dull
	6–11	Dull with luster along edges
	12-13	Dull with burn-on
5-6	1–5	Dull
	6–8	Dull with luster along edges
	9–10	Lustrous
	11–13	Lustrous with burn-on
7–10	1–5	Dull
	6	Semilustrous
	7-12	Lustrous
	13	Lustrous with burn-on
11-15	1–5	Dull
	6–7	Semilustrous
	8-10	Lustrous
	11–13	Lustrous with burn-on

Effect of propargyl alcohol on the outward appearance of tin coatings *

* Electrolyte composition $(g l^{-1})$: SnSO₄ 50, H₂SO₄ 100, synthanol 2; formalin 6 ml l⁻¹; mechanical agitation.

** c_{pa} is the concentration of propargyl alcohol.

concentrations of less than 2 g l^{-1} (1 g l^{-1}), the working interval of current densities for obtaining lustrous coatings becomes much narrower. At synthanol concentrations exceeding 3 g l^{-1} (4 g l^{-1}), the range of current densities yielding lustrous coatings remains unchanged, but electrolyte frothing is much enhanced,



Fig. 1. (*1*–6) Cathodic polarization curves of tin, measured on a rotating disk electrode, and (7, 8) capacitance *C* of electric double layer vs. electrode potential E_c in tin-plating electrolytes. (i_c) Current density. Electrolyte composition (g l⁻¹): SnSO₄ 50, H₂SO₄ 100. (*1*, 7) electrolyte; (2, 8) 1 + 2 g l⁻¹ synthanol, 6 ml l⁻¹ formalin, and 7 ml l⁻¹ propargyl alcohol; (*3*, *4*, *5*, *6*) 2 at disk electrode rotation rates of, respectively, 200, 500, 1000, and 2000 rpm.

which hinders electrodeposition in an agitated electrolyte.

In addition to the influence of organic substances, the study was concerned with effect of the $SnSO_4$ concentration on the working range of current densities for obtaining lustrous coatings. The investigation was carried out in an electrolyte containing 2 g l^{-1} synthanol, 6 ml l⁻¹ formalin, and 7 ml l⁻¹ propargyl alcohol. It was found that lowering the SnSO₄ concentration makes narrower the i_c range in which lustrous coatings are obtained. For example, lustrous coatings are obtained in the ranges $i_c = 2-5$ and 6-10 A dm⁻² at SnSO₄ concentrations of, respectively, 10-20 and 30 g l⁻¹. The H₂SO₄ concentration in the electrolyte should be within $90-100 \text{ g l}^{-1}$. At concentrations lower than $90 \text{ g} \text{ l}^{-1}$ the electrolyte is unstable in operation and the i_{c} range in which lustrous coatings are obtained becomes narrower. At H₂SO₄ content exceeding 100 g l^{-1} the range of current densities at which lustrous coatings are obtained remains unchanged.

It should be noted that high-quality lustrous coatings are only obtained in an agitated electrolyte, with dull deposits formed otherwise.

The current efficiency (CE) by tin in electrolytes yielding lustrous coatings decreases with increasing i_c and grows as the SnSO₄ concentration becomes higher. CE = 95–75% at SnSO₄ content of 10–20 g l⁻¹ and $i_c = 2-5$ A dm⁻², and CE = 95–90% at SnSO₄ content of 30–50 g l⁻¹ and $i_c = 6-12$ A dm⁻².

To reveal the influence of organic substances on electrodeposition of tin, cathodic polarization curves were measured on a rotating disk electrode. As seen in Fig. 1, the cathodic polarization is enhanced in the presence of organic substances, with a plateau of limiting current observed in the cathodic polarization curve (curves 1 and 2). With the disk electrode rotated, the $i_{\rm lim}$ value grows and the cathodic polarization decreases (curves 2-6). The limiting current in the polarization curves is associated with adsorption of organic substances and formation of an adsorption layer on the cathode surface. This assumption is confirmed by measurements of the capacitance of the electric double layer. As seen in Fig. 1 (curves 7 and 8), introduction of organic substances into the electrolyte makes the capacitance of the electric double layer lower. At potentials $E_c = -0.3...-0.4$ V, it decreases from 32 to 10 μ F cm⁻². At higher cathode potentials, organic substances are desorbed from the electrode surface and the continuity of the adsorption layer is broken, which leads to an increase in the electric double layer capacitance.

Figure 2 presents the degree of coating luster and surface coverage θ as functions of the current density. It can be seen that the degree of coating luster passes through a maximum, and the coverage decreases steadily, with increasing current density (curves *1* and *2*). The θ value at i_c yielding lustrous coatings ($i_c = 7-12 \text{ A dm}^{-2}$) varies between 35.0 and 27.7%. It should be noted that lustrous coatings can be obtained in an electrolyte with organic additives only in a certain range of i_c and θ . Presumably, the optimal values of these parameters correspond to the conditions in which the growing deposit has the minimum roughness.

The leveling power P was measured in a tin plating electrolyte as a function of the cathode current density (Fig. 2, curve 3). It can be seen that the tin plating electrolyte with organic additives produces leveling effect. With increasing i_c , the P value grows and, at $i_c = 10-11$ A dm⁻², passes through a maximum (P = 0.98). At present, the mechanism of surface leveling is commonly explained in terms of the adsorption-diffusion theory [4] whose main concepts are as follows. All leveling additives inhibit electrodeposition of metals, with the degree of inhibition controlled by diffusion as a result of the diffusion-controlled expenditure of the additives in the course of electrolysis. According to [4], polarization curves measured at different rates of disk rotation on a rotating disk electrode model qualitatively the cathodic process of microprojections (fast rotation) or microdepressions (slow rotation). The uneven accessibility of the microprofile is the reason for nonuniform distribution of the supply rate of organic substances to different parts of the microprofile. Since the inhibiting influence exerted by leveling additives on the process of metal electrodeposition grows with increasing rate of additive's diffusion toward the cathode (fast rotation), this effect is manifested to a greater extent on microprojections, and to a lesser extent in microdepressions, which leads to a nonuniform distribution of the electrodeposition rate.

It was proposed on the basis of this circumstance to assess the action of various additives by measuring the cathode potential in an electrolyte with additive(s) in two agitation modes [4]. If the polarization grows with increasing speed of electrode rotation, then it would be expected that additive(s) will exert leveling influence under the given conditions.

Analysis of the cathodic polarization curves in a tin plating electrolyte, measured on a rotating disk electrode (Fig. 1, curves 3-6), shows that they do not model the distribution of the electrodeposition rate



Fig. 2. (1) Degree of coating luster, L, (2) surface coverage θ , and (3) degree of leveling, P, vs. cathode current density i_c . Electrolyte composition (g l⁻¹): SnSO₄ 50, H₂SO₄ 100, synthanol 2; formalin 6 ml l⁻¹; propargyl alcohol 7 ml l⁻¹. Mechanical agitation.

over the microprofile. The probable reason is that an adsorption layer of organic substances is formed on the electrode surface. Intensification of the hydrodynamic mode affects the process of formation and disintegration of such a layer. In this case, the rate of tin deposition grows on all parts of the microprofile, i.e., changes in such a way that this appears outwardly just like a manifestation of the antileveling effect.

It should be noted that the same phenomenon is observed in electrodeposition of a Sn–Sb alloy from a sulfate electrolyte in the presence of synthanol, formalin, and 2-butyne-1,4-diol, or synthanol, formalin, and coumarin [5].

The leveling in an electrolyte, in which an adsorption layer of organic substances is present on the electrode surface, can be accounted for on the assumption that this layer disintegrates with increasing speed of disk electrode rotation. This "strips" microprojections to a greater extent as compared with microdepressions. At the same time, a higher rate of supply of organic substances to microprojections is observed with increasing rate of electrode rotation, and the microprojections are more strongly inhibited than microdepressions, which leads to nonuniform distribution of the metal electrodeposition rate over the microprofile surface. The phenomenon of leveling is related to the luster of electroplated coatings, since luster formation is also a process of surface leveling. The leveling eliminates large microirregularities 0.2 to 100 µm and more in size; in luster formation, very fine submicroirregularities (of size about 0.15 µm and less) are smoothed out [6].

Thus, submicro- and microirregularities of the cathode surface are smoothed out in a tin plating elec-

RUSSIAN JOURNAL OF APPLIED CHEMISTRY Vol. 75 No. 2 2002

trolyte containing synthanol, formalin, and propargyl alcohol.

Finally, it should be noted that the investigation performed made it possible to develop a sulfate acid tin-plating electrolyte of simple composition, which yields lustrous leveled coatings. The electrolyte composition is as follows (g l⁻¹): SnSO₄ 10–50, H₂SO₄ 90–100, synthanol (DS-10) 2–3; formalin (37% solution) 6–8 ml l⁻¹; propargyl alcohol 7–10 ml l⁻¹. The process is performed with mechanical agitation of the electrolyte, $i_c = 2-12$ A dm⁻². The current efficiency is 75–95%.

Agitation with air impairs the stability of the electrolyte operation because of the fast oxidation of the electrolyte. The electrolyte temperature is $18-25^{\circ}$ C. Above 25° C, the working i_{c} range in which lustrous coatings are obtained becomes narrower, electrolyte rapidly turns turbid, and a precipitate is formed on the bath bottom, which impairs the quality of the coatings obtained. The anodes should be made of pure tin. To prevent electrolyte contamination with sludge, the anodes are to be placed in sheaths of khlorin or propylene fabric.

The electrolyte is adjusted with respect to SnSO_4 , H_2SO_4 , and formalin, according to chemical analysis data [7]. The electrolyte adjustment with respect to synthanol should be done after 100 A h l⁻¹ is passed through the bath by adding 1 g l⁻¹ of synthanol. The expenditure of propargyl alcohol is 0.01 ml A⁻¹ h⁻¹.

CONCLUSIONS

(1) A study of tin electrodeposition from sulfate acid electrolyte with organic additives demonstrated that, in the case of simultaneous presence of synthanol, formalin, and propargyl alcohol, lustrous coatings are formed at $i_c = 2-12$ A dm⁻², depending on the SnSO₄ concentration in the electrolyte.

(2) Cathodic polarization curves were measured on a rotating disk electrode. It was found that organic substances inhibit electrodeposition of tin. In this case, a plateau of limiting current is formed in the polarization curve. With increasing speed of disk electrode rotation, the limiting current grows and the cathodic polarization decreases. (3) The degree of coating luster and the electrode surface coverage were measured in relation to the current density. It is shown that, with increasing i_c , the degree of luster grows and passes through a maximum, and the surface coverage decreases. The coverage varies between 35.0 and 27.7% in the range of current densities yielding lustrous coatings.

(4) The leveling power of a sulfate acid electrolyte with organic additives was studied. It is established that, in simultaneous presence of synthanol, formalin, and propargyl alcohol, the tin plating electrolyte shows positive leveling whose amount depends on i_c .

(5) The polarization curves obtained at different rates of disk electrode rotation cannot model the distribution of the rate of tin electrodeposition over the microprofile because of the sensitivity of the adsorption layer inhibiting the electrodeposition process to the hydrodynamic mode.

REFERENCES

- 1. Medvedev, G.I. and Gorbunova, I.M., *Zh. Prikl. Khim.*, 1990, vol. 63, no. 4, pp. 807–812.
- 2. Medvedev, G.I. and Mashutina, G.G., *Zh. Prikl. Khim.*, 1992, vol. 65, no. 4, pp. 789–795.
- Valentelis, L.Yu., Kamuntavichene, I.Yu., and Matulis, Yu.Yu., *Tr. Akad. Nauk LitSSR*, *Ser. B*, 1970, vol. 63, no. 4, pp. 129–136.
- Kruglikov, S.S., *Itogi nauki i tekhniki: Khimiya. Elektrokhimiya* (Advances of Science and Technology: Chemistry. Electrochemistry), Moscow: VINITI, 1965, pp. 117–151.
- Medvedev, G.I., Kruglikov, S.S., and Fursova, N.Yu., Gal'vanotekhn. Obrab. Poverkhn., 2000, vol. 7, no. 2, pp. 25–29.
- Gnusin, N.P. and Kovarskii, N.Ya., Sherokhovatost' elektroosazhdeniya poverkhnostei (Irregularity of Electrodeposition on Surfaces), Novosibirsk: Nauka, 1970.
- Vyacheslavov, P.M. and Shmeleva, N.M., *Kontrol'* elektrolitov i pokrytii (Monitoring and Control of Electrolytes and Coatings), Leningrad: Mashinostroenie, 1965.